# Fused-ring Borazines

J. J. HARRIS AND B. RUDNER

*Research Department, Koppers Research Center, Monroeville, Pennsylvania*

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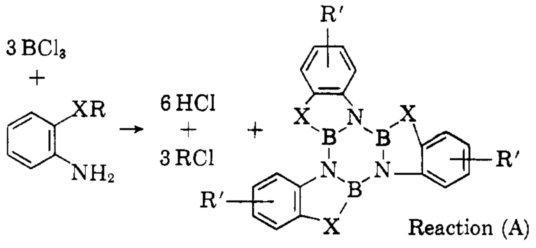
Fused-ring borazines are readily obtained from the reaction of trichloro- or tribromoborane with aniline *ortho*-substituted by amino, alkoxy, hydroxy, or mercapto groups. They are high melting compounds relatively insoluble in most solvents, and thermally stable to 300–400°.

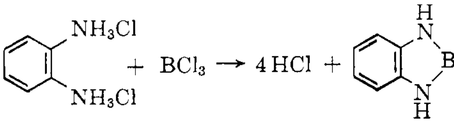
The recent disclosures[1–3] of tetracyclic fused-ring borazines prompt us to publish some of our work on these compounds. We have discovered that trichloro- or tribromoborane reacts readily with anilines *ortho*-substituted by amino, alkoxy, hydroxy or mercapto groups to yield, as final products, the *sym*-triazatriborinotrisbenzazaboroles,[4] I (see Table I for R′ values).



Reaction (A)

I

The compounds prepared are listed in Table I. By the recommended nomenclature system, the compound Ia ($X = O$; $R' = H$) becomes *s*-triazatriborino(2,1-*b*:4,3-*b*′:6,5-*b*″)tris(1,3,2)-benzoxazaborole.[4] This heterocycle and its analogue (Ie; $X = NH$, $R' = H$) have also been prepared by the action of trimethyl borate on *o*-aminophenol and *o*-phenylenediamine,[3] respectively. *o*-Phenylenediamine has also been converted[5] to 1,3-dihydro-2-chloro-1,3,2-benzodiazaborole[4] II under conditions similar to those reported here.



Reaction (B)

II

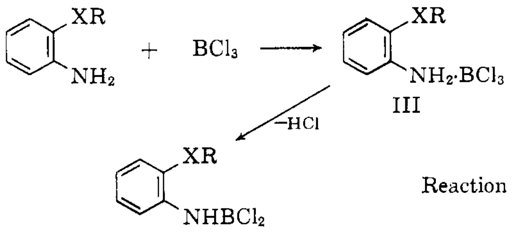
Either tribromo- or trichloroborane converted *o*-anisidine or *o*-aminophenol, in refluxing chlorobenzene, to compound Ia; $X = O$, $R' = H$ in an 80–85% yield. Under similar conditions, *o*-phenetidine gave a 12.5% yield of Ia. In refluxing benzene, trichloroborane and *o*-phenetidine gave largely polymeric intermediates (average molecular weight approximately 1000) that were convertible to Ia only on heating at higher temperatures.

Product Ia could be formed at 60° by treating the adduct formed by *o*-phenetidine and trichloroborane in chlorobenzene with 2,6-lutidine. Use of tertiary amines in the preparation of haloborazines has been reported.[6]

By reaction A, 2-methoxy-5-methylaniline, 2,5-dimethoxyaniline, and 5-chloro-2-methoxyaniline gave the respective 2,9,16-trisubstituted compounds (Ib to Id), inclusive, in Table I. The benzothiazaborole analog (If) was similarly prepared from *o*-aminobenzenethiol. Trichloroborane and bi-*o*-anisidine, in refluxing chlorobenzene, readily gave an incompletely cyclized, insoluble gray-green polymer.

The reaction product from trichloroborane and 5-nitro-2-anisidine could not be obtained analytically pure. An attempt to prepare an isomeric product from 4-nitro-2-anisidine yielded only tar. An unstable solid was obtained from trichloroborane and 2-amino-3-hydroxyanthraquinone. Hard polymers were obtained from trichloroborane and either 2-methoxyethyl- or 3-methoxypropylamine; these products are believed to contain no borazine rings, since they showed no spectral absorption bands between 6.7 and 7.3 μ.[7]

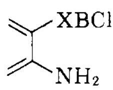
The first steps in the formation of I by the over-all reaction A are believed to involve dehydrohalogenation of the initial adduct III to an unstable arylaminodichloroborane IV:



III

IV

Reaction (C)

The alternative formation of  is re-

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[1] R. J. Brotherton, U. S. Patent 2,948,751, August 9, 1960.

[2] A. L. McCloskey, *et al.*, 135th National Meeting of the American Chemical Society, Boston Mass., April, 1959, 88M.

[3] R. J. Brotherton and H. Steinberg, *J. Org. Chem.*, **26**, 4632 (1961).

[4] Name recommended by Chemical Abstracts Nomenclature Service, Dr. Leonard T. Capell.

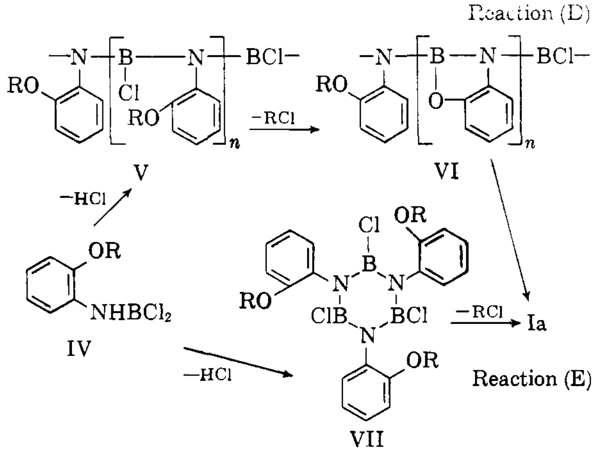
[5] L. F. Hohnstedt and A. M. Pellicciotto, 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960, 11-O.

[6] H. S. Turner and R. J. Warne, *Chem. Ind.* (London), 526 (1958).

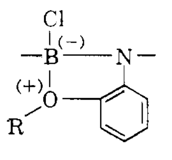
[7] K. Niedenzu and J. Dawson, *Angew. Chem.*, **71**, 651 (1959).

jected because trichloroborane, though known to cleave aromatic ethers,[8] is not known to cleave nonvicinal ether groups of alkoxyanilines[9] and because evolution of alkyl halide did not become apparent, in our experiments, before approximately half of the hydrogen halide indicated in Reaction (A) had been evolved.

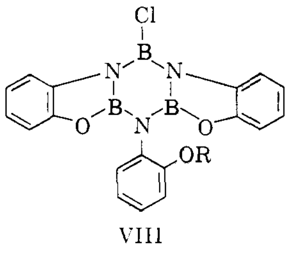
The unstable dehydrohalogenation products (IV, $X=O$; $R=H$, $CH_3$, $C_2H_5$) derived from phenols and ethers could form the fused ring products (Ia to Id) *via* either reaction D or reaction E:



In either case, borabenzoxazoline ring formation, as in the formation of VI from V, probably involves a highly favored intermediate such as



since ether cleavage has always been effected in good yield. This would explain not only the delayed and substantially complete evolution of alkyl halide, but also the absence of any incompletely cyclized borazines such as:



VIII

in the final product.

It is postulated that conversion of *o*-phenetidine to Ia goes *via* reaction D; the solvent-soluble major product obtained after reaction at about 80° gives analyses suggestive of a macrocyclic VI ($n=6$), and is convertible to Ia (in refluxing chlorobenzene) with relatively little ethyl chloride formation. In refluxing chlorobenzene the yield of Ia is low at completion of ethyl chloride evolution, also suggestive of reaction D. However, *o*-aminophenol or *o*-anisidine in refluxing chlorobenzene gave 83–84% yields of Ia upon completion of RCl evolution, indicating that these conversions followed reaction E.

After vacuum sublimation or recrystallization from chlorobenzene or nitrobenzene, the fused-ring borazines formed as asbestos-like mats of needles. All were high-melting, insoluble in nonpolar solvents, and apparently stable in air and atmospheric moisture. In wet acetone, ethanol, and dimethylformamide, the oxazolo analogs (Ia to Id) were readily hydrolyzed to boric acid and the expected *o*-aminophenol. Attempts to obtain partial hydrolysis or alcoholysis to N-tris(2-hydroxyphenyl)-B-trihydroxyborazine derivatives were unsuccessful.

Melting points, yields, and analyses are listed in Table I. Some of the analysis were somewhat low in carbon. Low carbon values in boron compounds have been reported by other workers.[10]

The infrared spectra were determined as Nujol mulls with a Perkin-Elmer Model 21 recording spectrophotometer. The data are tabulated in Table II. The bands appearing from 6.66–6.9 $\mu$ are assigned as boron–nitrogen ring stretching vibrations. This is a slightly lower wave length than is usually associated with this band in borazine[11–13] indicating a strongly bonded ring. The strong absorption at 8.0 to 8.14 $\mu$ in the oxygen containing rings are assigned to the phenyl-oxygen stretching frequency. The strong band appearing in all of the oxygen containing compounds (except the polymer from bianisidine, whose spectrum was difficult to obtain and is thus less reliable) at 8.48 to 8.67 $\mu$ is assigned to the boron to oxygen bond.

The B—O bond has been reported[14] to absorb at 7.52 $\mu$ for compounds of type $(RO)_2B{\cdot}NR_2$, and at 7.88 $\mu$ for compounds of type $RO{\cdot}B(NR_2)_2$. Our assignment of the B—O absorption to a considerably higher wave length is based on weakening of the bond and a consequent decrease in absorption frequency caused by distortion in the five-membered boroxazole ring. Strain is indicated since Fisher–Hirschfelder–Taylor models cannot be constructed for the compounds. These borazines also have a moderate to strong band, appearing in most cases with a weak band or shoulder at slightly higher frequency, at 13.99–14.4 $\mu$. These bands have been suggested as B—N ring deformation and useful for infrared confirmation of borazine.[15]

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(8) W. Gerrard and M. F. Lappert, *J. Chem. Soc.*, 1486 (1952).

(9) C. R. Kinney and C. L. Mahoney, *J. Org. Chem.*, **8**, 526 (1943).

(10) R. L. Letsinger and S. B. Hamilton, *J. Am. Chem. Soc.*, **81**, 3009 (1959).

(11) H. Watanabe, *Spectrochim. Acta*, **16**, 78 (1960).

(12) V. H. J. Baker and S. Frick, *Z. anorg. allgem. Chem.*, **295**, 83 (1958).

(13) W. Gerrard, *Spectrochim. Acta*, **18**, 149 (1962).

(14) D. W. Aubrey, M. F. Lappert, and H. Pyszora, *J. Chem. Soc.*, 5239 (1960).

(15) D. W. Aubrey, M. F. Lappert, and H. Pyszora, *ibid.*, 1931 (1961).

TABLE I

COMPOUNDS PREPARED, MELTING POINTS, AND ANALYTICAL DATA[a]

| Starting, aniline | Product Formula, color | Product M.p. (°C.)[b] | Product Yield, % th. | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | Boron, % Calcd. | Boron, % Found | Nitrogen, % Calcd. | Nitrogen, % Found | Other Calcd. | Other Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | (Ia) | | | | | | | | | | | | |
| 2-Hydroxy, | $C_{18}H_{12}B_3N_3O_3$ | 321–324[c] | 84 | 61.64 | | 3.48 | | 9.25 | | 11.98 | | ... | |
| or | white | | | | 61.73 | | 3.60 | | 9.34 | | 12.15 | | ... |
| 2-methoxy | (Ib) | | | | | | | | | | | | |
| 2-Methoxy-5- | $C_{21}H_{18}B_3N_3O_3$ | 337–340 | 31 | 64.20 | | 4.62 | | 8.26 | | 10.70 | | ... | |
| methyl- | white | | | | 64.09 | | 4.72 | | 8.10 | | 10.66 | | ... |
| | (Ic) | | | | | | | | | | | | |
| 2,5-Dimethoxy | $C_{21}H_{18}B_3N_3O_6$ | 274–276 | 50 | 57.21 | | 4.12 | | 7.36 | | 9.53 | | ... | |
| | white | | | | 55.6 | | 4.03 | | 7.48 | | 9.12 | | ... |
| | | | | | | | | | | | | Chlorine, % | |
| | (Id) | | | | | | | | | | | | |
| 5-Chloro-2- | $C_{18}H_9B_3Cl_3N_3O_3$ | 365–367 | 85 | 47.61 | | 2.00 | | 7.15 | | 9.25 | | 23.4 | |
| methoxy | white | | | | 47.05 | | 2.02 | | 6.96 | | 9.29 | | 23.15 |
| | (Ie) | | | | | | | | | | | | |
| 2-Amino- | $C_{18}H_{15}B_3N_6$ | 365[d] | 82 | 62.16 | | 4.35 | | 9.33 | | 22.16 | | ... | |
| | pale yellow | | | | 61.26 | | 4.28 | | 9.77 | | 23.34 | | ... |
| | | | | | | | | | | | | Sulfur, % | |
| | (If) | | | | | | | | | | | | |
| 2-Mercapto- | $C_{18}H_{12}B_3N_3S_3$ | 370–373 | 95 | 54.19 | | 3.03 | | 8.14 | | 10.53 | | 24.11 | |
| | white | | | | 54.22 | | 2.93 | | 8.44 | | 10.63 | | 24.38 |

[a] Analysis by Galbraith Microanalytical Laboratories, Knoxville, Tennessee. [b] Sealed capillary. [c] Reported melting point 210–280°.[3] [d] Reported as white solid decomposing at 380–390°.[3]

TABLE II

INFRARED SPECTRA DATA[a,b]

| Ia | Ib | Ic | Id | Ie | If[c] | Polymers from bi-*o*-anisidine |
|---|---|---|---|---|---|---|
| | | | | 2.91 m | 3.3 vw | |
| 6.20 m | 6.18 m | 6.15 m sh | 6.20 m | 6.25 m | 6.32 m | |
| -6.25 m | | 6.20 s | | | | |
| 6.58 vs sh | 6.56 s sh | 6.62 vs | 6.66 vs | 6.63 vs | 6.81 s | |
| 6.66 vs | 6.63 vs | 6.76 vs | 6.90 vs | 6.77 vs | 7.11 vs | 6.95 vs |
| | 6.85 vs | | | 6.86 vs | 7.20 vs | |
| 7.45 m | | | | | | |
| 7.92 m | 7.85 w | 7.83 m | 7.80 w | 7.81 s | | |
| | | | | 7.99 s | 8.12 s | 8.00 m |
| 8.11 s | 8.06 s | 8.04 m | 8.14 s | 8.35 m | 8.54 s | |
| | | 8.36 s | 8.55 m | 8.53 m | 8.65 m | |
| 8.66 s | 8.48 s | 8.57 vs | 8.67 s | | 8.81 m | |
| | 8.81 mw | | | | | |
| 9.13 m | 9.01 mw | 9.7 s | 9.39 m | | 9.45 m | |
| 9.81 s | 9.90 mw | 9.94 m | 9.93 m | 9.80 m | 9.70 m | 9.8 s |
| 10.80 m | | | | | | |
| | | 11.8 m | | | 11.75 m | 11.66 s |
| 11.70 m | | 12.1 m | | | | 12.37 s |
| 12.7 m | 12.5 s | 12.43 ms | 12.43 m | 13.30 s | 13.36 sh | 13.53 s |
| | | | | 13.54 vs | | |
| 13.40 vs | | | | 13.64 vs | 13.48 vs | 14.0 s |
| 14.19 w | 14.16 m | 13.52 m | 14.2m | 14.36 m | 13.99 s | 14.25 m |
| 14.39 s | 14.35 s | 14.4 s | 14.35–0.55 m | 14.51 m | 14.5 m | 14.63 m |

[a] By R. Mainier, this laboratory. [b] Determined as Nujol mulls. [c] Determined in halocarbon to 7.5.

## Experimental

**Starting Materials.**—Matheson's technical grade trichloroborane was distilled from the cylinder into chilled tared traps, then used directly. The tribromoborane was decolorized before use by being shaken with mercury. The anilines were purchased; *o*-anisidine and *o*-phenetidine were vacuum distilled while *o*-aminophenol was reprecipitated from its clarified, de-aerated hydrochloric acid solution with sodium bicarbonate.

**Product Ia. i. From *o*-Anisidine.**—A 2-l., three-necked flask, equipped with immersion thermometer, Dewar condenser kept at −78°, a gas-tight stirrer, and a water cooled reflux condenser topped with a Dewar condenser (at −78°) that was vented through a Dry Ice–chilled trap and a mineral oil bubbler, was charged with 137 g. (1.11 moles) *o*-anisidine in 1.1 l. of chlorobenzene. Trichloroborane (134 g., 1.14 moles) was condensed dropwise into the stirred solution, kept below 50° during an hour. Both Dewar condensers were brought to room temperature and the stirred suspension was heated. At approximately 60°, the initial adduct started to dissolve, and hydrogen chloride evolution became noticeable. Gas evolution ceased after the reaction mixture had been refluxed for almost 7 hr.; methyl chloride evolution and product precipitation were most pronounced during the second half of the reflux period. The trap contents, 73 g., were a mixture of hydrogen chloride, methyl chloride (90% of theoretical), and a trace of trichloroborane, identified by mass spectrographic analysis. The first crop of Ia was obtained by filtration at room temperature, the second after addition of an ether wash to the filtrate; total crude weight after being vacuum dried, 109.5 g., (84%). Vacuum sublimation at 300–330° and 1–5 mm. gave colorless needles in asbestoslike mats, m.p. 321–324°.

A similar reaction, in which tribromoborane was added through a pressure-equalized funnel to the stirred *o*-anisidine solution, gave an 84% yield of Ia after 5 hr. of reflux time. Methyl bromide (90%) appeared in the trap only after approximately half the theoretical amount of hydrogen bromide had been collected.

ii. **From *o*-Aminophenol.**—A 4-hr. reflux period was sufficient to convert the adduct of 71 g. (0.65 mole) of *o*-aminophenol and 80 g., (0.68 mole) of trichloroborane in 1 l. of chlorobenzene to 64 g. (84%) of product Ia. The initial adduct, formed immediately and exothermally, remained dissolved; hydrogen chloride evolution was accompanied by slow product precipitation all during reflux.

iii. **From *o*-Phenetidine.**—Under conditions described in i, 147 g. (1.07 moles) of *o*-phenetidine and 129 g. (1.10 moles) of trichloroborane gave 74 g. of mixed ethyl chloride and hydrogen chloride as volatile products and, as precipitate, 15.3 g. (12.5%) of product Ia. Evaporation of the filtrate at 2–10 mm. and 100° gave (after washing with ethyl ether and drying) 120.3 g. of granular white solid, m.p. 205–210°, that liberated hydrogen chloride upon exposure to air. This solid, held 1 hr. at 310° and 5 mm., lost approximately 15% of its weight in being converted to Ia.

A second run was made, using 66.6 g. (0.485 mole) of *o*-phenetidine and 58.7 g. (0.50 mole) of trichloroborane in 1 l. of refluxing benzene. Although after 8 hr. no more ethyl chloride was evolved, the cooled reaction mixture contained only small amounts of Ia. Vacuum evaporation of the filtrate left 65 g. of tan foam, softening without definite melting at 105°, containing 3.55% hydrolyzable chlorine, and having molecular weight (ebullioscopic benzene) of 1040. A macrocycle obtainable from VI ($n$ = 6) of linear formula $C_{42}H_{33}B_7ClN_7O_7$ would have a calculated molecular weight of 959 and a chlorine content of 3.7%. A portion of the foam, when refluxed 24 hr. in chlorobenzene, was converted to Ia, with only a minor quantity of ethyl chloride evolution.

A mixture of 137.3 g. (1.00 mole) of *o*-phenetidine and 117.2 g. (1.00 mole) of trichloroborane in a liter of chlorobenzene was stirred overnight at room temperature, then treated with 120 g. (1.12 moles) of 2,6-lutidine. The mixture was stirred at 60°, then cooled and filtered to give, as a precipitate, a mixture of lutidine hydrochloride and Ia. A considerable yield of incompletely cyclized product remained in the filtrate.

The other products, Ib to If, were obtained by refluxing chlorobenzene suspensions of the corresponding trichloroborane–aniline adduct for 8–13 hr., then working up as previously described. Compound Ic was obtained in the stated yield only by holding the solvent insoluble product at 300–350° and 0.5–5 mm. until no more sublimation occurred (about 12 hr.). The gray-green insoluble polymer, obtained from 0.95 mole of trichloroborane and 0.425 mole of bi-*o*-anisidine, contained residual chlorine indicative of only 90% cyclization.

**Reaction of Trichloroborane with 3-Methoxypropylamine or 2-Methoxyethylamine.**—The reaction of 137 g. (1.14 moles) of trichloroborane with 101 g. (1.14 moles) of 3-methoxypropylamine in refluxing chlorobenzene gave methyl chloride and a hard, tacky solid insoluble in the reaction medium. No chlorobenzene soluble products were found in the solvent. No sublimate formed when the solid was heated to 259° at reduced pressure. Elementary analysis indicated a B–N–Cl ratio of 1.0:0.83:1.25. A broad absorption band at 3.7–4.2 μ indicated that the product contained amine hydrochloride. Similar results were obtained with 2-methoxyethylamine.

**Acknowledgment.**—We wish to acknowledge our indebtedness to Dr. Philip Brumfield and Mr. James Morrison for some of the laboratory work reported here.

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# Carbodiimides. III. Conversion of Isocyanates to Carbodiimides. Catalyst Studies

JOHN J. MONAGLE[1a]

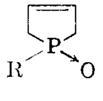
*Organic Chemicals Department, E. I. du Pont de Nemours & Co., Wilmington, Delaware*

*Received July 2, 1962*

Oxides and sulfides from a number of organic compounds of Group V-B and Group VI-B elements are effective catalysts for converting organic isocyanates to carbodiimides.

Carbodiimides have been prepared from isocyanates in excellent yield under mild conditions by the catalytic action of the phosphine oxides I and II[1b]:

$$2RNCO \xrightarrow{\text{I or II}} RN{=}C{=}NR + CO_2$$



I. R = $C_2H_5$
II. R = $C_6H_5$

A mechanism study[2] indicated that the reaction proceeded through the formation of an intermediate phosphinimide III which formed carbodiimide by reaction with a second molecule of isocyanate. The initial step in the reaction is believed to be a nucleophilic attack of the oxygen atom of the polarized phosphorus–oxygen bond in the catalyst on the isocyanate carbonyl:

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[1] (a) Present address: New Mexico State University, University Park, N. M. (b) T. W. Campbell and J. J. Monagle, *J. Am. Chem. Soc.*, in press.

[2] J. J. Monagle, T. W. Campbell, and H. F. McShane, Jr., *J. Am. Chem. Soc.*, in press.